Thermal Characterization of Poly(phenylene sulfide) Oligomers

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ABSTRACT: Oligomeric poly(phenylene sulfide)s (PPS's) prepared via the melt reaction of sulfur with excess *p*-diiodobenzene have been prepared and examined. We speculate that a transition from chain-folded crystals for longer chains in the PPS samples of this work to a different type such as extended-chain crystals for shorter chains occurs at 20 dp. This appeared to be substantiated by not only the T_m but also the T_{cc} and crystal reorganization peak data vs dp. The rate of crystallization seemed only to depend on oligomer length with the rate being faster at the shorter lengths, implying that addition of a chain to the growing crystal was limited mostly if not solely by viscosity effects and not the crystal habit. The crystallization from the glass (T_{ch}) increased as a function of the logarithm of dp. Evidence was also seen for the inability to adequately quench samples to a completely glassy state; the shorter the chain the more difficult the quench. A relationship for T_g vs oligomer length was also obtained which showed that a plateau level was reached at ~80 dp and was a linear function of log (dp) below that point, with a possible further increase in slope in the region of 10 dp and below. This relationship will provide a useful calibration against which other samples can be measured to estimate their dp. T_g^{∞}, which we suggest is 98 °C, is determined at significantly shorter chain lengths for this crystalline system than is seen for many reported amorphous systems.

Introduction

We have reported previously that poly(phenylene sulfide) (PPS) containing controlled levels of disulfide linkages and a wide range of molecular weights can be prepared in the melt by a new and novel process involving melt reaction of *p*-diiodobenzene and sulfur.[1,2] Both the molecular weight and the presence of disulfides affects the crystallization characteristics of the resultant polymer. Crystallization behavior of commercial PPS has been studied by Jog and Nadkarni,[3] Lovinger, Davis, and Padden,[4] Lopez and Wilkes,[5–8] Song, White, and Cakmak,[9] and Chung and Cebe.[10] A good review of what has been learned from all but the most recent work has been published by Lopez and Wilkes.[11] All of these studies concerned the crystallization of modest molecular weight materials over a relatively narrow range of molecular weights. In the course of probing the limits of reactant stoichiometry on polymer properties in our new melt reaction process, we have prepared PPS oligomers with iodoaryl termination that were of interest to study for themselves to determine relationships between chain length and thermal characteristics for shorter chains of PPS and a wider range of molecular weights than has been previously reported. Some of our initial work on such materials is reported here.

Experimental Section

Samples for this work with a dp of 40 or less were prepared with higher than normal excesses of *p*-diiodobenzene (DIB) in the preparation (excesses of ca. 25 mol % or less are normal) but using the same apparatus and temperature and pressure vs time profile as previously reported.[1] Excess DIB employed for all samples reported here ranged from 16.9 to 52.9 mol %. The polymer dp was calculated from the elemental analysis of the materials and was directly related to the DIB excess employed for the reaction.

DSC was measured on a DuPont 9900 thermal analyzer at a scan rate of 20 °C/min. Samples for the heating scan (ca. 10 mg) were melted at 320 °C for 2 min and then quenched on a metal block cooled in dry ice giving the T_g, the crystallization from the glass, T_{ch}, and T_m. Upon reaching 325 °C, the samples were then cooled at 20 °C/min and the crystallization exotherm observed upon cooling from the melt, T_{cc}, was recorded. Percent carbon, hydrogen, sulfur, and also iodine in the sample were determined via standard combustion analyses but employing a longer than standard combustion time.

Results and Discussion

The samples (Table I) studied were in the range from ca. 10 to almost 200 dp with most of them concentrated in the area of ca. 60 dp or less. For all preparations where DIB excesses employed in the reaction were above 25%, the polymer went solid in the latter stages of the melt preparation at 250 °C. This appears from our past experience to be characteristic of oligomers in that very high crystallization rate and crystallization temperature from the melt are obtained.[12] Solidification begins at the stirrer shaft, where the melt is somewhat cooler and the entire sample is soon solid. Solid-state polymerization of such samples removes the remaining excess *p*-diiodobenzene. In the solid-state operation, *p*-iodophenyl sulfide is detected[13] as the major component in the white crystals collected on the cool portion of the tube. The typical DSC heating scan for samples with 60 dp or greater from the glassy state and also cooling from the melt are given for reference in Figure 1 for a 66-dp sample.

The DSC measurements on the sample series (Table I, Figure 2) showed a peak value for T_m vs dp at ~40 dp with a very gradual decrease at higher degrees of polymerization. Below ~40 dp there was a decrease in T_m which became even more pronounced below ~20 dp. The decrease above 40 dp could be partly due to the expected decrease in T_m with increasing molecular weight but was no doubt mostly related to increasing disulfide levels with increasing dp. Since there is no evidence of any disulfides in the polymers at or below 40 dp from elemental analysis of the oligomers, the decrease in T_m below that point would seem to be simply related to crystal perfection. It also seems reasonable to assume that iodoaryl end groups and their increasing concentration with the shorter chains could magnify the effect of chain-end defects. It is apparent that at some point crystallites of PPS must change from chain-folded crystallites to another crystal type such as extended-chain crystals at the oligomer lengths shorter than necessary for chain folding to occur. The slope change at 20 dp for T_m is suggested to represent this crystal-type change and implied a natural fold length for PPS crystals

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Table I
PPS Oligomers

sample	T_g, °C	T_{ch}, °C	T_{cc}, °C	T_m, °C	% C	% H	% S	% I	rings
1	[a]	75	222	259	55.50	3.06	22.57	19.097	9.2
2	48	86	229	268	56.90	3.21	23.99	15.783	11.7
3	65	104	242	279	57.55	3.72	26.03	10.244	18.8
4	66	106	226	279	60.46	3.32	26.08	10.269	19.7
5	64	107	234	279	59.83	3.43	26.87	10.012	20.0
6	73	116	240	282	61.81	3.39	27.54	7.285	28.9
7	75	122	233	282	61.91	3.45	27.93	6.643	31.8
8	79	125	228	280	62.96	3.59	27.80	5.566	38.8
9	81	131	226	284	63.27	3.55	28.03	5.529	39.3
10	89	142	226	282	63.52	3.69	29.37	3.559	61.9
11	91	147	221	281	63.88	3.68	29.53	3.358	66.0
12	92	155	206	276	64.41	3.70	29.98	2.101	107.0
13	94	157	201	277	64.82	3.51	29.53	2.094	108.0
14	94	190	173	269	65.32	3.52	29.79	1.527	149.6
15	94	197	145	266	64.74	3.71	29.22	1.242	182.6
16	94	[a]	[a]	[a]	65.21	3.57	30.48	1.224	186.6

[a] No transition detected in the DSC scan.

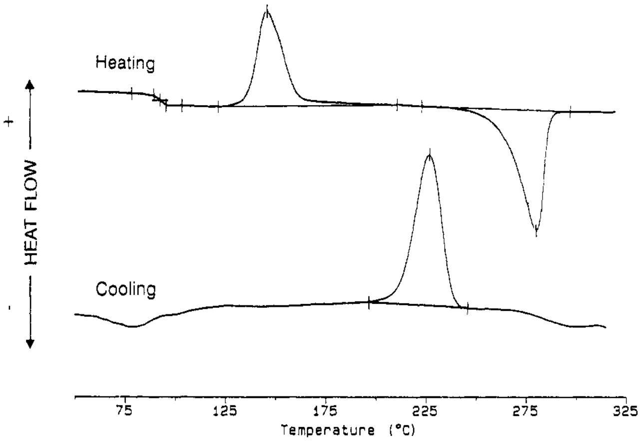

Figure 1. DSC scans of 66-dp PPS sample.

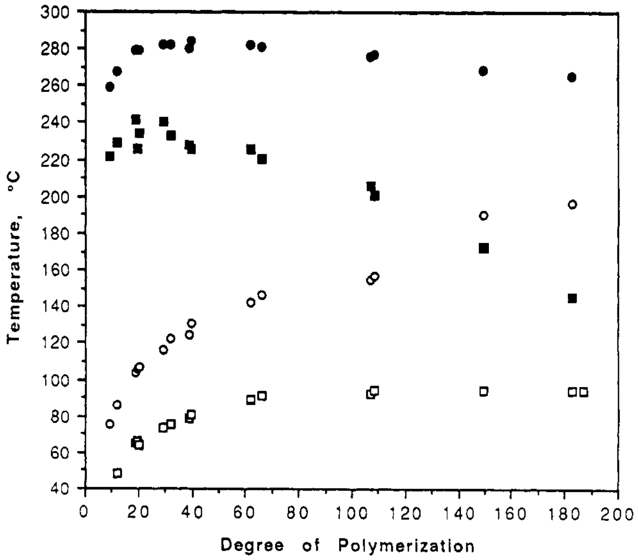

Figure 2. DSC transitions vs degree of polymerization: □, T_g; ○, T_{ch}; ■, T_{cc}; ●, T_m.

of some regular multiplier of 20 monomer units. Small-angle X-ray experiments to verify this will be reported separately.

The peak temperature of crystallization from the melt, T_{cc}, went through a maximum in the range of 20–30 dp with the decrease of the value being more rapid at the lower dp's and less rapid above that dp range. We speculate that this peak at low dp was also related to a change in crystal type for PPS at that point with the region below the peak being extended-chain-type crystals and the area above being folded-chain ones. For the higher dp polymers, T_{cc} decrease was not only a function of increasing chain entanglements but also disulfide content, which increased with increasing dp for polymers of greater than 100 dp. The peak crystallization temperature from the glass, T_{ch}, by contrast to the above observations showed only an increase with increasing dp. It was found to correlate linearly with the logarithm of the degree of polymerization (Figure 3). This again is consistent with shorter chains showing greater proportional effects from the chain ends interfering more with the crystallization process. It is of interest to note that the quantity $T_{cc} - T_{ch}$ (Figure 4), which can be thought of as a relative rate of crystallization of the sample, showed a monotonic decrease with increasing dp. This implied that the rate of addition of a chain to the growing crystal may be strongly related simply to the medium viscosity and was apparently independent of the crystal habit. The same conclusion is reached by looking at the data as the relative undercooling of T_{cc} vs T_m (Figure 5), which was also only a function of the oligomer chain length. Crystal growth rate studies are in progress to more fully examine the interpretation of these data.

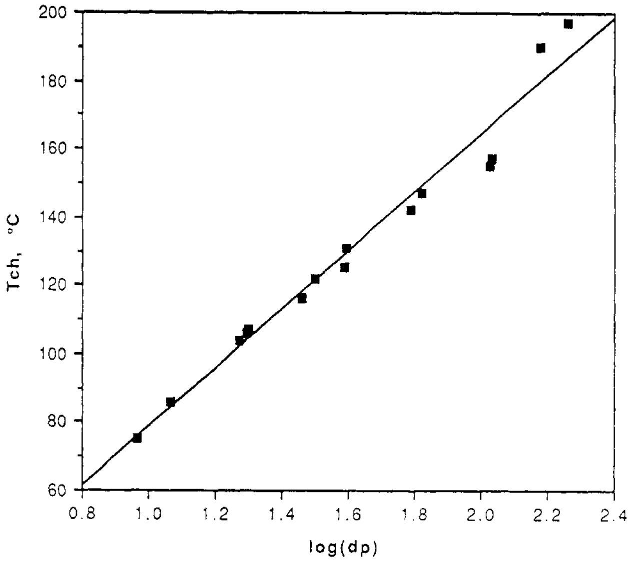

Figure 3. T_{ch} vs degree of polymerization.

Where the average chain length of the samples was 20 or less, an exothermic peak occurred just immediately prior to the onset of the T_m (Figure 6). The position of the peak decreased in temperature with decreasing oligomer length while increasing in area at the same time. A 20-dp oligomer

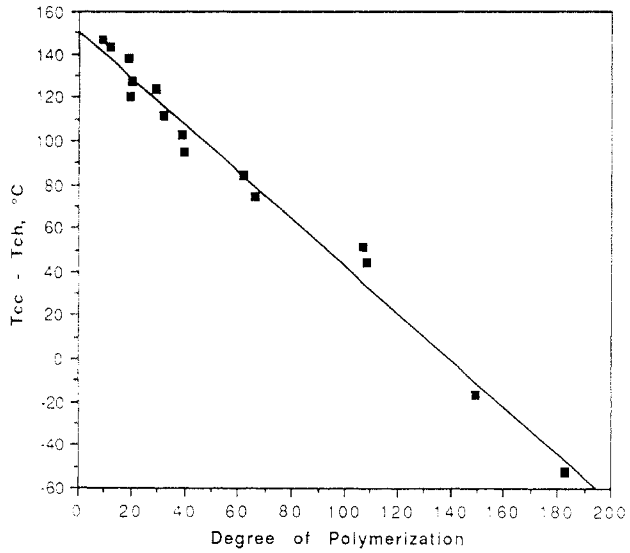

Figure 4. $T_{cc} - T_{ch}$ vs degree of polymerization.

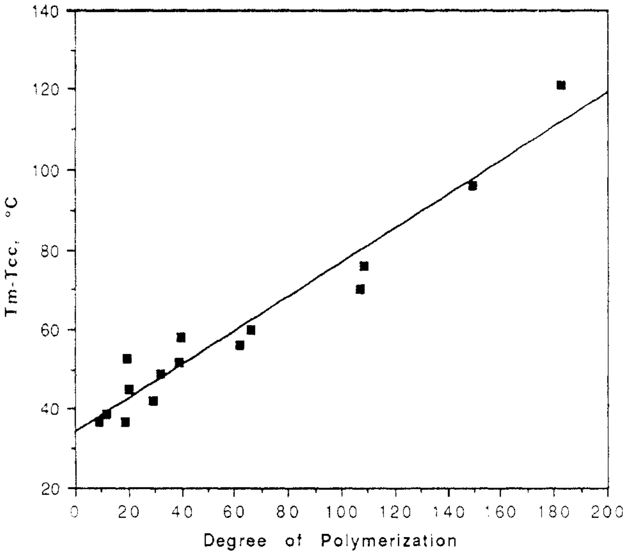

Figure 5. Relative undercooling vs oligomer dp.

appeared to be about the limit of detection for this peak. Although a very small peak was observed at 20 dp, no apparent trace of it could be seen on the DSC scans for 30 dp and higher oligomers. This exothermic peak, which is probably a crystal reorganization process taking place immediately prior to the melt, was less than one-tenth the area of the T_m at the largest, which area increased relative to T_m as the dp decreased.[14] The small area of this crystal reorganization when added to the crystallization on heating exotherm (Table II) relative to that of the melting peak implies a high degree of crystallinity/local order already existed in the samples prior to reaching that temperature. The fraction of the heat evolved at T_m that can be accounted for by the combination of these two exotherms was a dramatic function of the oligomer length (Figure 7). Thus, as chain length decreased, the rate of crystallization increased, causing complete quenching to be more difficult in accord with the observation discussed above of the monotonic increase in the difference of $T_{cc} - T_{ch}$ with decreasing average chain length. The resultant crystals are, as expected, increasingly imperfect as the chains shorten, as evidenced by increasingly broader T_m's along with their lower peak values. It is worth noting again that the crystal reorganization peak appears at the suggested point of change from one crystal habit to another.

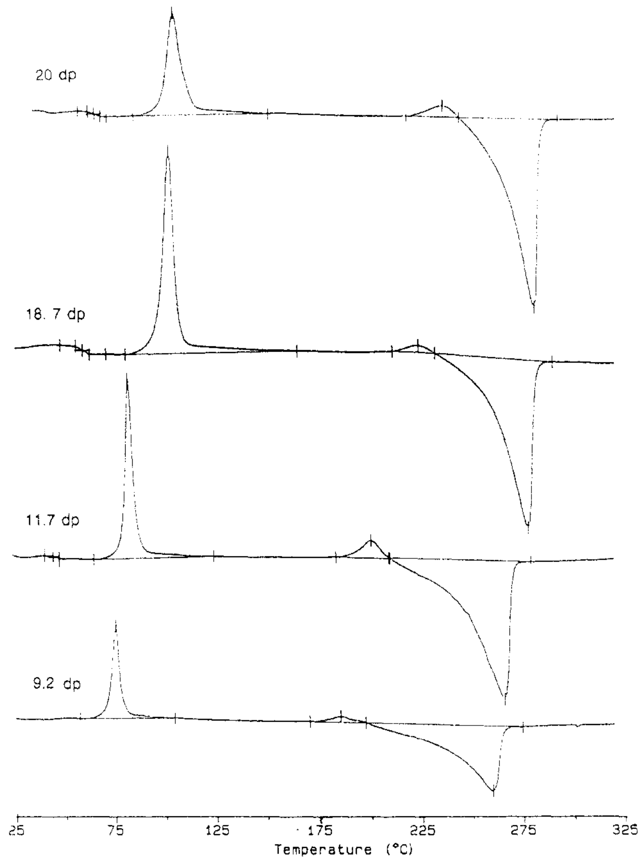

Figure 6. DSC heating scan of quenching PPS oligomers.

The observation of only ca. 75% of the heat of fusion for T_m being accounted for in the maximum case reported here is consistent with other PPS samples of commercial materials we have measured. For example, the following ratios of the heats for T_{ch} to those for T_m were observed: Ryton P4 0.81, Ryton PR06 0.80, Ryton V-1 0.63, Fortron PPS 0.74. We ascribe this to an inability to completely quench to the glassy state even for these modest molecular weight materials.

The crystal reorganization observations along with the amount of heat that can be accounted for as a function of oligomer length have not been reported previously. The broad exotherm between the T_{ch} and the T_m of PPS seen by Chung and Cebe[10] when samples were annealed under varying conditions and times starting from the glassy state were not seen in our data. The crystal reorganization process and lowering of the amount of heat that can be accounted for that we observe here may involve both the inability to quench the samples completely and the presence of the rigid amorphous fraction in PPS reported by Cheng et al.[15] This rigid amorphous fraction is equivalent to the poorly organized regions that Chung and Cebe speculated possess short-range order but are not crystalline. A rigid amorphous fraction would, of course, result in lowering of the heat evolution observed upon heating of the samples. This is also consistent with the report of Jones, Mitchell, and Windle,[16] who suggested from wide-angle X-ray data and conformational calculations that the conformation of the isolated chain differs little between the crystalline and glassy states on higher molecular weight samples of PPS. Thus, with increasingly lower chain lengths and therefore chain mobility to increasingly lower temperatures, one would expect that an increasingly larger number of chains aggregate into small crystal regions with, of course, much lower melting points, owing to the high levels of imperfection of the

Table II
Relationship of Heats of T_{ch}, T_r, and T_m vs Chain Length

dp	$\Delta H(T_{ch})^a$	$\Delta H(T_r)^b$	$\Delta H(T_r)/\Delta H(T_{ch})$	$\Delta H_f(T_m)$	$(\Delta H(T_{ch}) + \Delta H(T_r))/\Delta H_f(T_m)$
9.2	2.637	1.326	0.335	14.75	0.269
11.7	6.058	0.542	0.082	15.13	0.436
18.9	6.395	0.667	0.096	14.31	0.494
20.0	7.47	0.550	0.074	14.29	0.561
66.0	6.537			8.89	0.735

[a] All heats are given in calories per gram. [b] Crystal reorganization peak.

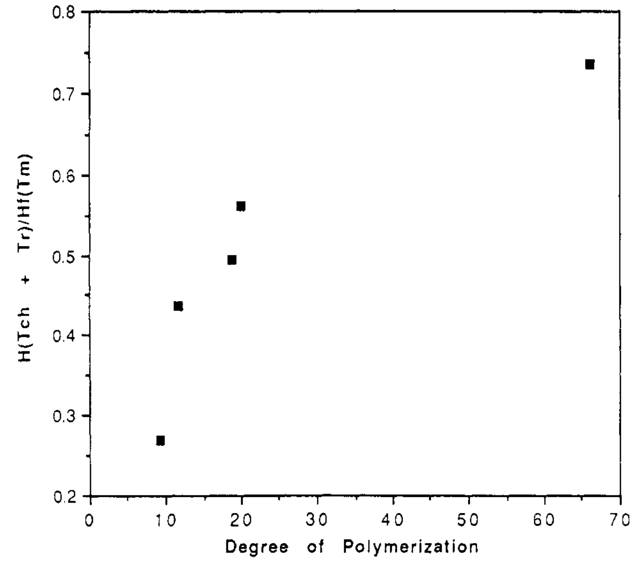

Figure 7. Fraction of H_f at T_m accounted for by T_{ch} and crystal reorganization (T_r).

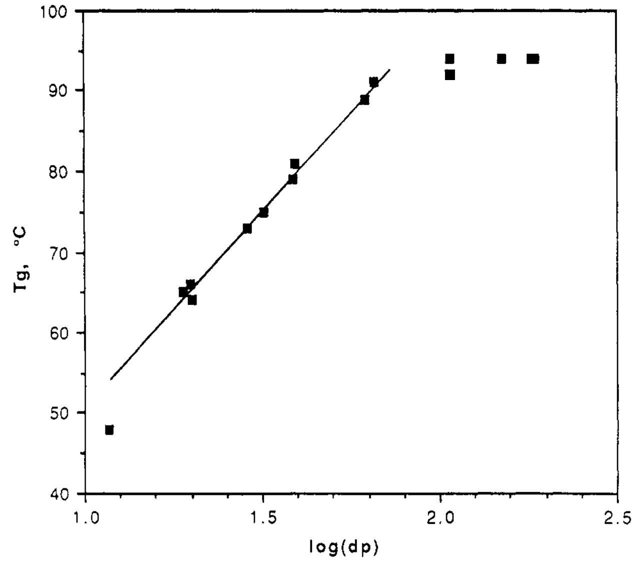

Figure 8. T_g vs log (dp).

crystallites. This is consistent especially with our observations on the relative crystallization rate vs oligomer dp.

The glass transition temperature did not reach a plateau value of ~94 °C until a dp of ~80 (Figure 8) but thereafter remained essentially constant. Cowie[17] has analyzed a number of polymers by correlating the T_g with the logarithm of the degree of polymerization and found that there are three distinct regions: region I is essentially the plateau where T_g is no longer a function of molecular weight, region II is where T_g shows a large dependence on molecular weight, and region III is where an even more marked increase in that relationship is seen as the material essentially approaches monomer characteristics. The data for PPS oligomers showed clear evidence for at least region I and region II since, below the plateau, T_g was a linear function of the logarithm of the degree of polymerization. The region II data had an excellent fit to a straight line. The T_g at 11 dp (lowest point on the plot) may represent the transition to region III behavior but the data were obviously insufficient to verify that. The transition of region I to region II behavior was also not exact as data in that range were not obtained but can be calculated from the equation for region II behavior to be 77 dp. The range spanned by the region I data is not sufficient to establish that as the T_g^∞ for this polymer. Using the equations given by Cowie[17] relating the region II to region I transition would give a T_g^∞ of 108 °C and would also give a transition from region III to region II at 10.8 dp. Huo and Cebe[18] have recently reported a maximum T_g in highly crystallized PPS of 108 °C. In our experience,[19] samples of PPS having melt viscosities in the range of (1–1.5) × 10^6 P melt viscosity showed a T_g of 98 °C. We suggest this value as more representative of T_g^∞ than the calculated value. Using this latter value would give a region III to region II transition at 10.6 dp, which is the same as the prediction of the Cowie equations.[17] Further support for a 98 °C value for T_g^∞ was obtained by plotting T_g vs the reciprocal of the number-average molecular weight,[20] which gave an intercept of 99 °C. It should be noted here that the shortest oligomer was 9.2 dp, which could not be induced to give a glass transition temperature indication in the DSC. The expected T_g for a 9.2-dp oligomer would be in the area of 45 °C. In spite of extensive efforts at quenching and searching for a low T_g, apparently the sample was of such a crystalline and/or highly ordered nature that there was insufficient amorphous region to be able to see the signal in the DSC trace. The exact nature of order for such samples is an area that is of interest for further study.

The transition from region II to region I behavior for these samples was at a much lower dp than expected on the basis of the data reported by Cowie[17] for amorphous systems, where this transition was increased by increasing polymer T_g. Crystallinity of the samples is most probably the cause of this large effect on how early the II to I transition occurs in PPS. This implies that for crystalline polymers the intermolecular environment sufficient to determine T_g^∞ is determined at significantly shorter chain lengths than in an amorphous system.

Conclusions

We speculate that a transition from chain-folded crystals for longer chains in the PPS samples of this work to a different type such as extended-chain crystals for shorter chains occurs at 20 dp. This appeared to be substantiated by not only the T_m but also the T_{cc} and crystal reorganization peak data vs dp. The rate of crystallization seemed only to depend on oligomer length with the rate being faster at the shorter lengths, implying that addition of a chain to the growing crystal was limited mostly if not solely by viscosity effects and not the crystal habit. The crystallization from the glass (T_{ch}) increased as a function of the logarithm of dp. Evidence was also seen for the inability to adequately quench samples to a completely glassy state; the shorter the chain the more difficult the quench. A relationship for T_g vs oligomer length was also obtained which showed that a plateau level was reached at ~80 dp and was a linear function of log (dp) below that point, with a possible further increase in slope in the region of 10 dp and below. This relationship will provide a useful calibration against which other samples can be measured to estimate their dp. T_g^∞, which we suggest is 98 °C, is determined at significantly shorter chain lengths for this crystalline system than is seen for many reported amorphous systems.

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